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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY WASHINGTON, D.C. 20460

JAN 30 1986

MEMORANDUM

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

SUBJECT:

Methamidophos Registration Standard: Addendum #1

FROM:

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TO:

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and

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Attached is addendum # 1 to the Residue Chemistry chapter of the methamidophos Registration Standard which was completed on 2/19/82. This addendum was produced by DYANAMAC Corporation.

The projected return date for this addendum is February 7, 1986.

This addendum provides a reply to a response to deficiencies discussed in the Residue Chemistry chapter of the methamidophos Registration Standard submitted by Chevron Chemical Company and dated September 27, 1986.

This addendum contains no confidential information.

If you need additional information please advise.

cc: A. Barton, HED

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Subject File

Reading File

Methamidophos Registration Standard File

RDI: RBPerfetti: 1/29/86: RDSchmitt: 1/29/86: x 557-7484



Final Report

Methamidophos

Task 4: Addendum #1. Registration

Standard-Residue Chémistry Chapter

Contract No. 68-02-4226

January 17, 1986

Submitted to:

Environmental Protection Agency Arlington, VA 22202

Submitted by:

Dynamac Corporation Enviro Control Division The Dynamac Building 11140 Rockville Pike Rockville, MD 20852



METHAMIDOPHOS ADDENDUM #1

RESIDUE CHEMISTRY

Task 4

INTRODUCTION

Chevron Chemical Co. submitted new and revised residue chemistry data in response to data requirements listed in the data gap tables of the methamidophos Registration Standard as set forth in the RCB chapter dated February 19, 1982. The specific data requirements, the registrant's response, and our comments and conclusions are detailed below. Also considered in this addendum are changes and/or additions to the methamidophos guidance document presented in an EPA memorandum dated July 25, 1985 by W.J. Hazel (Methamidophos Registration Standard, Additional Data Requirements).

<u>Footnote 1 data requirements</u>: Brussels sprouts, cucumbers, and melons. Either residue data for aerial applications are needed or labels must be submitted to prohibit aerial applications.

Registrant's response - Brussels sprouts: Chevron Chemical Co. submitted new data from a single test conducted in CA in which Brussels sprouts received six weekly aerial applications of the 4 lb/gal SC/L formulation at 1 lb ai/A in 3-10 gal/acre. Residues of methamidophos per se were 0.02 ppm in or on two samples harvested 14 days after the final treatment. Samples were stored for ~50 days at -20 C prior to analysis using a GC method (RM-12A-6).

Our comments and conclusions: The test state of CA contains 87% of the U.S. Brussels sprouts acreage harvested (1982 Census of Agriculture, Vol. 1, p. 338); thus geographic representation is adequate. Residue analysis was accomplished using the previously unsubmitted analytical method RM-12A-6. This method involves extraction with ethyl acetate, cleanup using silicated column chromatography and measurement by GC using either a rubidium

sulfate thermionic detector or a flame photometric detector operating in the phosphorus mode. In a single determination, recovery from Brussels sprouts was 88% at a fortification level of 0.1 ppm. We consider this method adequate for data collection. We conclude that registered use of methamidophos formulations, including aerial applications, will not result in residues in excess of the 1 ppm tolerance. No additional data are required for this topic.

Registrant's response - cucumbers: Chevron Chemical Co. has submitted a label revision to the state of FL (FL810043) which includes the statement, "Apply by ground equipment only".

Our comments and conclusions: We consider this issue resolved; no additional data are required for this topic.

Registrant's response - melons: Chevron Chemical Co. submitted new data from tests (the number of tests per state is given in parentheses) conducted in AZ(1), FL(2), GA(2), IN(1), MS(1) and TX(6) where canteloupe and watermelon received five foliar applications at weekly intervals with the 4 lb/gal SC/L formulation at 1.5 lb ai/A (1.5x the maximum registered rate). Aerial equipment was used only in one FL and one TX test on watermelons. Samples were harvested at various intervals following the last application and separated into peel and pulp fractions prior to analysis. Residue values in or on whole fruit were calculated from peel and pulp data based on the weight of each sample. Calculated residues of methamidophos per se in or on canteloupe were 0.19-1.43 ppm (5 samples) at 0 days, 0.21-0.93 ppm (5 samples) at 7 days, and 0.19-0.56 ppm (5 samples) at 14 days after the final treatment. Calculated residues of methamidophos per se in or on watermelon (ground equipment) were 0.01-0.62 ppm (six samples) at 0 days, 0.06-0.55 ppm (five samples) at 7 days, and 0.01-0.18 ppm (six samples) at 14 days after the final treatment. Applications using aerial equipment resulted in residues of methamidophos per se in or on watermelons (2 samples/interval) calculated on a whole fruit basis of 0.34-1.07 ppm at 0 days, 0.16-0.26 ppm at 7 days, and 0.04-0.50 ppm at 14 days after the final treatment. Residue analysis was accomplished using a GC method designated Report No. 34047.

Chevron Chemical Co. also submitted a revised label for use of methamidophos on melons in FL (FL810034) which changes the PHI for watermelon from 7 days to 14 days to coincide with that established for cantaloupe and honeydew melons. The type of equipment to be used is not specified.

Our comments and conclusions: Although the data reflecting aerial applications are minimal and of limited value. Since exaggerated rates (1.5x the maximum registered rate) were used and the resulting residues in or on watermelons at the 14-day PHI did not exceed the established 0.5 ppm tolerance level, this information is adequate to support the established tolerance for melons when methamidophos is applied via aircraft. No futher information is required.

Footnote 2 data requirements: Data describing residue levels in outer leaves are required because those leaves are used (as wrapping) during the transportation of a commodity in interstate commerce. Additional data requirements put forth in an EPA memorandum by W.J. Hazel dated July 25, 1985 are reproduced here verbatim:

cabbage must receive <u>several</u> (depending on local agricultural practice) treatments with an EC at 1 lb ai/A at test sites in CA, FL, NY, TX, and WI. Labels permit applications as needed at 7-day intervals. Heads bearing all or most wrapper leaves (as heads may be shipped interstate) must be analyzed at least 35 days (the PHI) after the last treatment for methamidophos. Both aerial and ground equipment must be used.

Registrant's response: Chevron Chemical Co. presented the argument that data reflecting residue levels in cabbage wrapper leaves should not be required because they are not a raw agricultural commodity per se. They maintain such a requirement would set a precedent for other commodities. Nonetheless, Chevron submitted data from single tests conducted in FL and CA. Residues of methamidophos per se were nondetectable (<0.01 ppm) in or on four samples of trimmed whole cabbage heads and nondetectable (<0.01 ppm) to 0.13 ppm in or on four samples of whole untrimmed cabbage heads harvested 35 days following the last of six foliar applications (ground equipment) at weekly intervals with the 4 lb/gal SC/L formulation at 1 lb

ai/A. Samples were stored for about 45-90 days at -20 C prior to analysis using GC method RM-12A-6.

Our comments and conclusions: The newly submitted data from CA and FL test sites are insufficient to support the established tolerance for residues in or on cabbage (with wrapper leaves) because no aerial applications were made and no trials were conducted in TX (15%), WI (8%), and NY (13%); percentage of acreage harvested as quoted in the 1982 Census of Agriculture, Vol. 1, p. 339 appear in parentheses. The following additional data are required:

o Residues in or on cabbage heads (including all or most wrapper leaves) harvested 35 days after the last of six applications at 7-day intervals with the 4 lb/gal SC/L formulation at 1 lb ai/A. Both ground and aerial equipment must be used. Tests must be conducted in TX, WI, and NY since these states represent major cabbage production areas (1982 Census of Agriculture, Vol. 1, p. 339).

It should be clarified that analysis of cabbage heads with wrapper leaves does not refer to cabbage wrapper leaves as an r.a.c. per se but refers to untrimmed cabbage heads, i.e. bearing thier wrapper leaves.

Footnote 3 data requirements: The available residue data for cauliflower do not support the established tolerance because application methods were not specified. Existing petitions must be supplemented with this information or the data must be replaced.

Registrant's response: Chevron Chemical Co. submitted data from one new study (T-6231) conducted in CA. Residues of methamidophos per se in or on two samples each of trimmed and untrimmed cauliflower heads were nondetectable (<0.01 ppm) and 0.03-0.05 ppm, respectively; samples were harvested 28 days after the last of six aerial applications with the 4 lb/gal SC/L formulation at 1 lb ai/A and stored for about 90 days at -20 C prior to analysis using method RM-12A-6.

Chevron Chemical Co. also submitted residue chemistry data which has been revised to include the previously unspecified application method. These data are summarized in Table 1.

Table 1. Residues of methamidophos in or on cauliflower following multiple foliar applications.

REPORT NO.	TEST LOCATION	NO. OF APPLICATIONS ^a	blīp _z	RESIDUE (ppm) ^C
35385	Ontario, Canada	8	14	0.03
35386	B.C., Canada	8	3	0.23
35779	NY	7	14	0.02
39073	NY	9	28	0.07
39075	NY	5	28	0.02
40775	AZ	6	28	0.04
40776	AZ	5-6	28	0.12
40890	CA	3	28	<0.01
40891	CA	5	14	0.11
40892	CA	3	27	0.05
41147	CA	5	28	<0.01
41527	NY	4	12	0.08-0.20
41528	NY	3	13	0.09
41529	NJ	15	21	0.19-0.23
41648	NY	7	21	<0.01

aApplications of the 4 lb/gal SC/L formulation were made using ground equipment (hand sprayer, tractor mounted sprayer or compressed air sprayer). The application rate was 1 lb ai/A in all tests except NY (38779) where the last two of five applications were at 2 lb ai/A and NY (41527) where all applications were at 0.5 lb ai/A.

bPTI = posttreatment interval (days) after the last application.

CResidues of methamidophos <u>per se</u> in or on cauliflower heads without leaves.

Our comments and conclusions: We note that residue data for cauliflower originally submitted by Chevron Chemical Co. (MRID 00014072; test nos. 1530, 1666, 1783, 1784, and 1898) and discussed in the Registration Standard reflect ground applications made with a tractor-mounted boom sprayer. The tests presented in Table 1 were available for review but not discussed in the Registration Standard. We find the newly submitted and revised residue data adequate to support the established tolerance of 1 ppm for residues of methamidophos in or on cauliflower. No additional data are required for this topic.

Footnote 4 data requirements: For tolerances on eggplant grown in Mexico, information on the application methods used in developing data previously submitted is not available. It must be submitted or the studies must be repeated and resubmitted. Data reflecting the use of the maximum application rate (1 lb ai/A) must also be submitted to support current tolerances for eggplant grown in the U.S.

Registrant's response: Chevron Chemical Co. submitted new data pertaining to residues of methamidophos <u>per se</u> from four FL tests in which eggplant received 3-17 foliar applications (made using ground equipment) of the 4 lb/gal SC/L formulation at 1 lb ai/A. Residues were nondetectable (<0.01 ppm) to 1.9 ppm 3 days, 0.03-0.65 ppm 7 days, 0.02-0.15 ppm 14 days, and 0.02-0.03 ppm 21 days after the final application. Samples were stored for 83-387 days prior to analysis using GC method RM-10. The registrant has submitted revisions to the existing state registration (FL 810033) specifying that applications are to be made using only ground equipment and has also proposed that use of the 4 lb/gal SC/L formulation on eggplant (EPA Reg. No. 239-2404) be added to the federal label but restricted to use in FL only.

Our comments and conclusions: We find the newly submitted data support the established tolerance for residues in or on eggplant treated with methamidophos in the United States (FL only). While reexamining data from previously submitted Mexican trials (Baychem Corporation; MRIDs 00014119, 00014120, 00014130, and 00014131), we noted that the method of application used in

these tests was available during the preparation of the Methamidophos Registration Standard. Up to 15 applications were made using ground equipment (three tests) and six early season aerial applications were followed by seven late season, ground-applied treatments (one test). No additional data are required for this topic.

Footnote 5 data requirements: Current data do not adequately support the established tolerance because they do not describe residues on head lettuce with most or all of the wrapper leaves intact (as it is typically transported in interstate commerce). These data must be supplemented or replaced.

Registrant's response: Chevron Chemical Co. submitted Mobay Chemical Corp. document number AS 85-2318 pertaining to residues of methamidophos per se in or on lettuce harvested from two tests conducted in FL and four tests conducted in CA. Residues were nondetectable (<0.01 ppm) to 0.03 ppm in or on six samples of lettuce (whole heads) harvested 21-51 days after the last of 3-4 aerial applications with the 4 lb/gal SC/L formulation at 1 lb ai/A in a total volume of 3-20 gal/A. Applications were made when plants were at various growth stages: postemergence, 6-8 inches high, and heading. Residue analysis was accomplished using the thermionic emission GC method 34047.

<u>Our comments and conclusions</u>: We find the newly submitted data support the the established tolerance for residues of methamidophos in or on lettuce. No additional data are required.

Footnote 6 data requirements: Current data do not support the tolerance for use of methamidophos on peppers in Mexico. One of three samples exceeded the tolerance 14 days after the last application (the current preharvest interval is 14 days) and the maximum seasonal rate was not applied. Because current data show that residue levels fall to (or below) tolerance levels by 21 days after the last application, either an extension of the labeled PHI to 21 days must be made or data on the period between day 14 and day 21 will be accepted to determine a precise PHI at which residues will not exceed tolerance. New studies that reflect the maximum permitted application rate

must also be submitted, or labels must be modified to reflect the maximum rate tested.

Registrant's response: Mobay Chemical Co. has submitted revisions to SLN registrations NM820008 and TX820019 (Note: These 24 (c) registrations have been established since the Registration Standard for methamidophos was issued.). These labels permit multiple foliar applications of the 4 lb/gal SC/L formulation at 0.5 lb ai/A. Up to five applications may be made as needed up to 21 days before harvest.

Our comments and conclusions: The data submitted by Baychem Corp. (MRIDs 00014121, 00014122, 00014123, and 00014140) and reviewed in the Registration Standard reflect ground and aerial applications to peppers only at test sites in Mexico. These data are not sufficient to assess the adequacy of the established tolerance because they do not reflect the currently registered domestic uses. Therefore, the following additional data for these domestic uses are required:

o Peppers must receive five applications with the 4 lb/gal SC/L formulation at 0.5 lb ai/A at test sites in NM and/or TX.

Ground and aerial equipment must be used in separate tests. samples must be taken and analyzed for methamidophos 21 days after the final treatment.

Footnote 7 data requirements: In order to support the established U.S. tomato tolerance, data must be submitted from studies using the maximum application rate allowed by current labels, 1 lb ai/A, or the maximum label rate must be reduced to the level tested (0.5 lb ai/A per acre).

Registrant's response: Chevron Chemical Co. submitted new data pertaining to residues of methamidophos <u>per se</u> in or on tomatoes from tests conducted in CA(2), FL(2), IN(2), MI(2), NJ(1), OH(2), TX(3), VA(2), and Ontario, Canada(2); the number of tests per state are given parenthetically. Multiple foliar applications (at 7-day intervals) were made with the 4 lb/gal SC/L formulation at 1-2 lb ai/A. The type of equipment used (ground or aerial) was unspecified. At the 1 lb ai/A rate, residues in or on tomatoes (approximately nine samples per harvest interval) were 0.34-5.07 ppm 0 days, 0.12-2 ppm

3-6 days, 0.08-1.83 6-10 days, and 0.04-1.62 ppm 14 days after the final treatment. At the 2 lb ai/A rate (2x the maximum rate), residues in or on tomatoes (approximately eight samples per harvest interval) were 0.97-4.10 ppm 0 days, 0.22-8.15 ppm 3 days, 0.27-3.17 ppm 7 days, and 0.08-4.65 ppm 14 days after the final treatment. Samples were stored under unspecified conditions for about 30-120 days prior to analysis using a GC method designated Chemagro Report No. 34047.

Our comments and conclusions: The newly submitted data are inadequate to support the established 1 ppm tolerance for methamidophos residues in or on tomatoes because residue levels—1 ppm were observed and the method of application (ground or aerial equipment) was unspecified. We recommend that the registrant propose a tolerance increase from 1 ppm to 2 ppm and clarify the type of equipment used for foliar applications in these trials. We also note that no processing data were submitted; therefore the following additional data are required:

o Data reflecting residues in catsup, juice, wet and dry pomace, and puree processed from fruit bearing measurable, weathered residues. If residues are found to concentrate in any of these processed products, appropriate food/feed additive tolerances must be proposed.

Footnote 8 data requirements: Residue data are needed for alfalfa and clover grown for their seed because cuttings might be made for feed use and because germinating alfalfa seeds (sprouts) are used by humans for food.

Residue data are needed for carrots and table (garden) beets grown for their seed because roots and tops (of beets only) may be fed to livestock. In addition, residue data will be needed on carrots and table beets grown from the seed of previously treated crops.

Registrant's response: Chevron Chemical Co. is conducting a residue trial on alfalfa in which samples of cuttings and germinating seeds (sprouts) will be analyzed for residues of methamidophos. These data will be submitted to satisfy requirements for both alfalfa and clover. In regard to the data

requirements for carrots and garden beets, the registrant presents the argument that the dilution of methamidophos residues in or on carrots and garden beets grown from the seed of previously treated crops would preclude the necessity of such data.

Our comments and conclusions: The present non-food use classification for alfalfa and clover is inappropriate because following harvest of seed, subsequent cuttings for hay may be taken for livestock consumption. Therefore, based on the forthcoming data, appropriate tolerances must be proposed for alfalfa seed forage and hay and for clover forage and hay.

Data are still required for carrots and table (garden) beets. If the seed of these plants contains detectable residues following applications at registered rates, then the registrant must present data which demonstrate there is no likelihood of residues in these crops grown from the harvested seed.

In lieu of the data required above and as per our conclusion regarding non-food use classifications for 24 (c) registrations on vegetables grown for seed (Memo of 11/21/85, K. Arne to J. L. Auerbach), the two uses on carrots and table (garden) beets may be considered to be non-food provided that; 1) The registrant provides compelling reasons for such classification; and 2) That the states in which these 24 (c) registrations are valid will assume responsibility to insure that the seed crops will not be diverted to food or feed.

Footnote 9 data requirements: Residue data are needed for the processed products of peppers and tomatoes that require dehydration of the raw agricultural commodity.

Our comments and conclusions: Processed (dehydrated) peppers are no longer considered a significant processed product; therefore this data requirement has been eliminated. Processing data are required for tomatoes; refer to Footnote 7 for details of data requirements.

Additional comments: The subject of storage stability of methamidophos on frozen plant products was not addressed in the Methamidophos Registration Standard. This was noted in a memorandum dated July 25, 1985 by W.J. Hazel EPA, RCB, HED (Methamidophos Registration Standard; Additional Data Requirements). In conjunction with residue data submitted to satisfy the footnote data requirements described above, Chevron Chemical Co. submitted a storage stability study (designated report number 37444) conducted on broccoli, lettuce, cabbage, cauliflower, and Brussels sprouts. Chopped crop samples bearing measurable, weathered residues were stored at -20 C for 2-9 months and reanalyzed using the GC method RM-10. The range of recoveries presented in Table 2 represent two samples except for lettuce which represents three samples.

Table 2. Storage Stability of methamidophos in various crops.

Storage	Interval
DLULAGE	TILLET ACT

Crop	(months)	% recovery
Broccoli	7	86-92
	9	85-86
Lettuœ	2	50-88
Cabbage	5	100
-	8	100
Cauliflower	3	88-127
	6	67–83
Brussells sprouts	2	64-86
	5	60-75

We find these data indicate that residues of methamidophos <u>per se</u> are relatively stable for nine months during frozen storage.

No data were required for potatoes in the data gap tables of the Methamidophos Registration Standard (RCB's chapter dated February 19, 1982). However, upon reevaluation by RCB (refer to the above-cited memo by W.J. Hazel) the available residue data on potatoes (MRID 00014075) are not geographically

representative. The data requirements put forth by RCB are reproduced here, verbatim:

o "Potatoes grown in CO, ID, ME, ND, and WA must be treated repeatedly (according to local agricultural practices) with an EC product at 1 lb ai/A using both aerial and ground equipment. Labels permit applications as needed or in a 7- to 10-day program. Tubers are to be harvested at intervals including the 14-day PHI and analyzed for methamidophos. In addition, processing studies may be needed (granules, chips, and dried potatoes) to determine if food additive tolerances are necessary."